## What is claim

- 1. A composite solid polymer electrolyte membrane (SPEM) comprising a porous polymer substrate interpenetrated with an ion-conducting material, wherein the SPEM is substantially thermally stable to temperatures of at least about 100°C.
- 2. The SPEM of claim 1, wherein the SPEM is stable from at least about 100°C to at least about 175°C.
- 3. The SPEM of claim 1, wherein the SPEM is stable from at least about 100°C to at least about 150°C.
- 4. The SPEM of claim 1, wherein the SPEM is stable from at least about 120°C to at least about 175°C.
  - 5. The SPEM of claim 1 wherein
- (i) the porous polymer substrate comprises a homopolymer or copolymer of a liquid crystalline polymer or a solvent soluble thermoset or thermoplastic aromatic polymer, and
- (ii) the ion-conducting material comprises a homopolymer or copolymer of at least one of a sulfonated, phosphonated or carboxylated ion-conducting aromatic polymer or a perfluorinated ionomer.
- 6. A composite solid polymer electrolyte membrane (SPEM) comprising a porous polymer substrate interpenetrated with an ion-conducting material, wherein
- (i) the porous polymer substrate comprises a homopolymer or copolymer of a liquid crystalline polymer or a solvent soluble thermoset or thermoplastic aromatic polymer, and
- (ii) the ion-conducting material comprises a homopolymer or copolymer of at least one of a sulfonated, phosphonated or carboxylated ion-conducting aromatic polymer or a perfluorinated ionomer.

- 7. SPEM of claims 1 or 6, wherein to orous polymer substrate comprises a microinfrastructure substantially interpenetrated with the ion-conducting material.
- 8. The SPEM of claims 1 or 6, wherein the porous polymer substrate comprises an extruded or cast film.
- 9. The SPEM of claim 5, wherein the SPEM substantially stable to temperatures of at least about 100°C.
- 10. The SPEM of claims 5 or 6, wherein the liquid crystalline polymer substrate comprises a lyotropic liquid crystalline polymer.
- 11. The SPEM of claim 10, wherein the lyotropic liquid crystalline polymer substrate comprises at least one of a polybenzazole (PBZ) and polyaramid (PAR) polymer.
- 12. The SPEM of claim 11, wherein the polybenzazole polymer substrate comprises a homopolymer or copolymer of at least one of a polybenzoxazole (PBO), polybenzothiazole (PBT) and polybenzimidazole (PBI) polymer and the polyaramid polymer comprises a homopolymer or copolymer of a polypara-phenylene terephthalamide (PPTA) polymer.
- 13. The SPEM of claims 5 or 6, wherein the thermoset or thermoplastic aromatic polymer substrate comprises at least one of a polysulfone (PSU), polyimide (PI), polyphenylene oxide (PPO), polyphenylene sulfoxide (PPSO), polyphenylene sulfide (PPS), polyphenylene sulfide sulfone (PPS/SO<sub>2</sub>), polyparaphenylene (PPP), polyphenylquinoxaline (PPQ), polyarylketone (PK) and polyetherketone (PEK) polymer.
- 14. The SPEM of claim 13, wherein the polysulfone polymer substrate comprises at least one of a polyethersulfone (PES), polyetherethersulfone (PEES), polyarylethersulfone (PAS), polyphenylsulfone (PPSU) and polyphenylenesulfone (PPSO<sub>2</sub>) polymer; the polyimide (PI) polymer comprises a polyetherimide (PEI) polymer; the polyetherketone

(PEK) polymer prises at least one of a polyether one (PEK), polyetheretherketone (PEEK), polyetheretherketone (PEEK), polyetheretherketone-ketone (PEEKK) and polyetherketoneetherketone-ketone (PEKEKK) polymer; and the polyphenylene oxide (PPO) polymer comprises a 2,6-diphenyl PPO or 2,6 dimethyl PPO polymer.

- 15. The SPEM of claims 1 or 6, wherein the pore size of the porous polymer substrate is from about 10 Å to about 20,000 Å.
- 16. The SPEM of claim 15, wherein the pore size is from about 10 Å to about 2,000 Å.
- 17. The SPEM of claim 15, wherein the pore size is from about 500 Å to about 10,000 Å.
- 18. The SPEM of claims 1 or 6, wherein the ion-conducting material has an ion-conductivity from about 0.01 S/cm to about 0.50 S/cm.
- 19. The SPEM of claim 18, wherein the ion-conducting material has an ion-conductivity greater than about 0.1 S/cm.
- 20. The SPEM of claims 5 or 6, wherein the ion-conducting aromatic polymer comprises wholly aromatic ion-conducting polymer.
- 21. The SPEM of claims 5 or 6, wherein the ion-conducting aromatic polymer comprises a sulfonated, phosphonated or carboxylated polyimide polymer.
- 22. The SPEM of claim 21, wherein the polyimide polymer is fluorinated.
- 23. The SPEM of claim 20, wherein the sulfonated wholly-aromatic ion-conducting polymer comprises a sulfonated derivative of at least one of a polysulfone (PSU), polyphenylene oxide (PPO), polyphenylene sulfoxide (PPSO), polyphenylene sulfide (PPS), polyphenylene sulfide sulfone

(PPS/SO<sub>2</sub>), polyarylketone (PK), polyetherketone (PEK), polybenzazole (PBZ) and polyaramid (PAR) polymer.

## 24. The SPEM of claim 23, wherein

- (i) the polysulfone polymer comprises at least one of a polyethersulfone (PES), polyetherethersulfone (PEES), polyarylsulfone, polyarylethersulfone (PAS), polyphenylsulfone (PPSU) and polyphenylenesulfone (PPSO<sub>2</sub>) polymer,
- (ii) the polybenzazole (PBZ) polymer comprises a polybenzoxaxole (PBO) polymer;
- (iii) the polyetherketone (PEK) polymer comprises at least one of a polyetherketone (PEK), polyetheretherketone (PEEK), polyetherketone-ketone (PEKK) and polyetherketone-ketone (PEKKK) polymer; and
- (iv) the polyphenylene oxide (PPO) polymer comprises at least one of a 2,6-diphenyl PPO, 2,6-dimethyl PPO and 1,4-poly phenylene oxide polymer.
- 25. The SPEM of claims 5 or 6, wherein the perfluorinated ionomer comprises a homopolymer or copolymer of a perfluorovinyl ether sulfonic acid.
- 26. The SPEM of claim 25, wherein the perfluorovinyl ether sulfonic acid is carboxylic- (COOH), phosphonic- (PO(OH)<sub>2</sub>) or sulfonic- (SO<sub>3</sub>H) substituted.
- 27. The SPEM of claim 1, wherein the ion-conducting material comprises at least one of a polystyrene sulfonic acid (PSSA), poly(trifluorostyrene) sulfonic acid, polyvinyl phosphonic acid (PVPA), polyacrylic acid and polyvinyl sulfonic acid (PVSA) polymer.
- 28. The SPEM of claims 1 or 6, wherein the porous polymer substrate comprises a homopolymer or copolymer of at least one of a substituted or unsubstituted polybenzazole polymer, and wherein the ion-

conducting male al comprises a sulfonated derivation of a homopolymer or copolymer of at least one of a polysulfone (PSU), polyphenylene sulfoxide (PPSO) and polyphenylene sulfide sulfone (PPS/SO<sub>2</sub>) polymer.

- 29. The SPEM of claim 28, wherein the polysulfone polymer comprises at least one of a polyethersulfone (PES) and polyphenylsulfone (PPSU) polymer.
- 30. The SPEM of claims 1 or 6, wherein the SPEM has a specific resistance from about 0.02 to about 20  $\Omega$ \*cm<sup>2</sup>.
- 31. The SPEM of claims 1 or 6, wherein the SPEM has a specific resistance of less than about  $0.2~\Omega^*cm^2$ .
- 32. The SPEM of claims 1 or 6, wherein the SPEM has a thickness from about 0.1 mil. to about 5.0 mil.
  - 33. The SPEM of claim 32, wherein the thickness is about 1 mil.
- 34. A method of producing a composite solid polymer electrolyte membrane (SPEM) in accordance with claims 1 or 6, comprising the steps of preparing a mixture of a polymer substrate and an ion-conducting material in a common solvent and casting or extruding a composite membrane from the mixture.
- 35. A method of producing a composite solid polymer electrolyte membrane (SPEM) in accordance with claims 1 or 6, comprising the steps of preparing a mixture of the polymer substrate and the ion-conducting material and extruding or casting a composite film directly from the mixture.
- 36. A method of producing a composite solid polymer electrolyte membrane (SPEM) comprising the steps of performing a sulfonation reaction within the pores of a polymer substrate, wherein the SPEM is substantially thermally stable to temperatures of at least about 100°C.

- 37. ethod of producing a composite spolymer electrolyte membrane (SPEM) in accordance with claims 1 or 6, comprising the steps of solubilizing the ion-conducting polymer and imbibing the porous polymer substrate with the ion-conducting polymer.
- 38. A method of producing a composite solid polymer electrolyte membrane (SPEM) in accordance with claims 1 or 6, comprising the steps of preparing the polymer substrate and subsequently impregnating the substrate with appropriate monomers which are then polymerized in-situ to form the SPEM.
- 39. A device comprising a composite solid polymer electrolyte membrane in accordance with claims 1 or 6.
  - 40. The device of claim 39, wherein the device is a fuel cell.
- 41. The device of claim 40, wherein the fuel cell is a direct methanol fuel cell or a hydrogen fuel cell.
- 42. A method of decreasing methanol crossover rate in the fuel cell of claim 41 by using the SPEM of claim 1 in an electrochemical reaction in the fuel cell.
- 43. The device of claim 40, wherein the fuel cell is used to supply power to an electronic device.
- 44. The device of claim 39, wherein the device is a system for membrane-based water electrolysis or chloralkali electrolysis.
- 45. The device of claim 39, wherein the device is a dialysis, electrodialysis or electrolysis system.
- 46. The device of claim 39, wherein the device is a pervaporation or gas separation system.

- 47. device of claim 39, wherein the deep is a water splitting system for recovering acids and bases from waste water solutions.
- 48. The device of claim 39, wherein the device is an electrode separator in a battery.
- 49. The device of claim 41, wherein the methanol permeation rate in the direct methanol fuel cell is less than about 50mA/cm<sup>2</sup> of equivalent current density at 0.5V.
- 50. The SPEM of claims 1 or 6, wherein the ion-conducting material is crosslinked.